

ISOVALENCE SUBSTITUTIONS IN MULTICOMPONENT ALUMINATES $ABCO_4$

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The crystallochemical characteristics of polycrystalline samples, $Sr_{1-x}La_xAlO_4$, $Sr_{1-x}Nd_xAlO_4$ ($x = 0.02 \div 0.20$) and $Sr_{1-x}Bi_xNdAlO_4$ ($x = 0.05 \div 0.50$) prepared by the oxalate coprecipitation and cryochemical technique have been investigated. The existence limits of single-phase states for pairs of elements Sr-Pb ($x < 0.05$) and Nd-Bi ($x < 0.2$) were determined. The microprobe X-ray analysis showed the Bi uniform distribution. The dielectric properties of pure $SrLaAlO_4$, $SrLaGaO_4$ and partial replacement La→Nd samples were measured. It can be concluded that these compounds are suitable as substrate materials of HTSC thin films.

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Preparation of high quality substrate materials for HTSC-films is a subject of numerous investigations of the recent years [1-3]. Complex aluminates and gallates $ABCO_4$ -type, where A = Sr; B = La, Nd; C = Al, Ga, are (very perspective for these purposes) suitable substrates for these films.

The present paper deals with results of investigations of crystallochemical characteristics of polycrystalline samples $SrLaAlO_4$ (SLA), $SrNdAlO_4$ (SNA), $SrLaGaO_4$ (SLG) and the products of partial substitutions of Sr and La (Nd) by Pb and Bi. Samples were produced by the oxalate coprecipitation or cryochemical technique.

The phase compositions of the samples were determined by an X-ray analysis and the chemical compositions of some samples were investigated by a local microprobe analysis.

For revealing a possible homogeneity region of SLA compound in a ternary system $SrO-La_2O_3-Al_2O_3$ samples were synthesized with an excess of initial components (1-2 mol.%). All final products contain many phases and their lattice parameters did not change. So, we did not detect experimentally the homogeneity region of SLA compound. Thus, the structure of these compounds, probably, has strict dimensional restrictions. The formation of $ABCO_4$ -phase for yttrium is impossible what confirms our supposition. We tried to receive $SrBiAlO_4$, although the

experiments showed that this phase does not exist. Only the mixture of complex aluminates and bismuthates was found after thermal treatments.

Using the above-mentioned methods pure single phase aluminates and galates as well as doped products were received. We used two different approaches for doped products obtaining: the cation composition conservations ($\text{Sr}_{1-x}\text{Pb}_x\text{LaAlO}_4$, $\text{Sr}_{1-x}\text{Ba}_x\text{NdAlO}_4$, $\text{SrNd}_{1-x}\text{Bi}_x\text{AlO}_4$) and additions of superstoichiometric or substoichiometric quantities of cations (1–2 mol.%). Table I represents the final X-ray data. These values are in good agreement with literature data [4, 5].

TABLE I

X-ray data for doped complex aluminates.

Nominal composition	Lattice parameters		
	a [Å]	c [Å]	V [Å ³]
$\text{Sr}_{0.98}\text{Pb}_{0.02}\text{NdAlO}_4$	3.722(2)	12.48(1)	173.0(3)
$\text{Sr}_{0.95}\text{Pb}_{0.05}\text{NdAlO}_4$	3.722(4)	12.46(2)	173.0(6)
$\text{Sr}_{0.95}\text{Pb}_{0.05}\text{LaAlO}_4$	3.752(3)	12.617(10)	178.0(4)
$\text{Sr}_{0.9}\text{Pb}_{0.1}\text{LaAlO}_4$	3.757(3)	12.626(11)	178.2(4)
$\text{Sr}_{0.85}\text{Pb}_{0.15}\text{LaAlO}_4$	3.759(3)	12.634(10)	178.5(4)
$\text{SrNd}_{0.95}\text{Bi}_{0.05}\text{AlO}_4$	3.722(2)	12.48(2)	172.9(5)
$\text{SrNd}_{0.90}\text{Bi}_{0.10}\text{AlO}_4$	3.718(3)	12.49(2)	172.7(6)
SrLaAlO_4 [4]	3.755	12.62	
SrNdAlO_4 [5]	3.723	12.47	

TABLE II

Local microprobe analysis data.

Nominal sample composition	Point	Atomic elements relations			
		Al	Sr	Nd	Bi
$\text{SrNd}_{0.9}\text{Bi}_{0.1}\text{AlO}_4$	Aver. 5p.	1.00	0.998	0.95	0.10
			Al	Sr	Nd
$\text{Sr}_{0.95}\text{Pb}_{0.05}\text{NdAlO}_4$	Aver. 3p.	1.00	1.04	0.83	0.004

According to the local microprobe and thermogravimetric data (Table II) the mass loss in the cryochemical Bi- and Pb-containing samples during the thermotreatment was determined. This phenomenon is connected with the partial Pb and Bi evaporation; Pb-concentration decreases in about 10 and Bi — in 3–5 times. The samples are porous, the noticeable element segregation takes place. The oxalate samples keep an initial composition (10 at.% Bi) and uniform element distribution. Unfortunately, single phase Pb-containing products can be received by the oxalates precipitation: a temperature increase results in high Pb-evaporation.

In the case of the isoivalent partial replacement in SNA of Sr by Ba ($\text{Sr}_{1-x}\text{Ba}_x\text{NdAlO}_4$, $0.0 < x < 0.5$) any sample did not reach a single-phase state. In addition to the major phase SNA, X-ray reflections extra lines have been fixed on diffractogramms, the intensity of which increases with a quantity of Ba, some of these extra lines were identified as belonging to binary aluminates $\text{Sr}_2\text{Al}_2\text{O}_5$ and $\text{Sr}_4\text{Al}_2\text{O}_7$. In the limits of experimental error the lattice parameters and volumes of elementary cells $\text{Sr}_{1-x}\text{Ba}_x\text{NdAlO}_4$ did not change at the addition of Ba, it was possible to conclude to replace strontium by barium. When x exceeds 0.2, the SNA phase does not exist any more due to the additional interactions.

The ABCO_4 phase formation temperatures considerably decrease from 1500°C to 1000°C (Pb) and to 1200°C (Bi) by adding a small quantity of Pb (≈ 0.4 at.%) and greater amounts of Bi (5 and 10 at.%) to the samples. Probably, the initial component interaction occurs without formation of intermediate aluminates.

The crystal lattice parameter misfits between the substrate materials SLA, SNA and SLG and high temperature superconductors $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2212) were calculated. Maximal misfits of lattice parameters did not exceed 4%. The minimal values are observed for the gallium compound.

The electrophysical characteristics (dielectric constant (ϵ), dielectric loss ($\tan \delta$) and resistance (ρ)) of some synthesized materials were measured. For SLA at temperatures of 127.0–355.5 K the characteristic values varied in the following limits: $\epsilon = 17.14 \div 22.54$, $\tan \delta = 0.049 \times 10^{-3} \div 0.016 \times 10^{-3}$, $\rho = 2.72 \times 10^{12} \div 4.10 \times 10^{12} \Omega \cdot \text{m}$. For SLG: $\epsilon = 13.11$, $\tan \delta = 0.091 \times 10^{-3}$, $\rho = 5.32 \times 10^{10} \Omega \cdot \text{m}$.

An addition of a small excess quantity Nd_2O_3 (2.5 mol.%) to this material did not practically change the values of the characteristics ($\epsilon = 14.75$, $\tan \delta = 0.113 \times 10^{-3}$, $\rho = 5.81 \times 10^{10} \Omega \cdot \text{m}$).

The complex aluminates and gallates with received dielectric and electric properties were suitable as substrates for HTSC materials.

Crystals of SLA with Bi_2O_3 were grown by the Czochralski method from an initial mixture contained 1 at.% of Bi_2O_3 . The obtained crystals had a good quality and light yellow colour. The XRD and electron microprobe and chemical analysis were used to detect Bi. The only traces of Bi (lower than 10^{-5} wt.%) were found in the crystals. Results of XRD did not show any changes in the lattice parameters of pure SLA. The Bi_2O_3 is mainly deposited on cool parts of the growth chamber. The same results were obtained for SLG.

References

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